



Electron Affinity Calculations for Thioethers

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Prepared for the
1998 Annual Meeting
sponsored by the Society of Tribologists and Lubrication Engineers
Detroit, Michigan, May 17-21, 1998

National Aeronautics and
Space Administration

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This report is a formal draft or working paper, intended to solicit comments and ideas from a technical peer group.

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ABSTRACT

Previous work indicated that polyphenyl thioethers possessed chemical properties, related to their electron affinities, which could allow them to function as vapor phase lubricants (VPL). Indeed, preliminary tribological tests revealed that the thioethers could function as vapor phase lubricants but not over a wide temperature and Hertzian pressure range. Increasing the electron affinity of the thioethers may improve their VPL properties over this range. Adding a substituent group to the thioether will alter its electron affinity in many cases. Molecular orbital calculations were undertaken to determine the effect of five different substituent groups on the electron affinity of polyphenyl thioethers. It was found that the NO₂, F, and I groups increased the thioethers electron affinity by the greatest amount. Future work will involve the addition of these groups to the thioethers followed by tribological testing to assess their VPL properties.

Keywords: High temperature tribology; Vapor phase lubrication; Chemistry

INTRODUCTION

In order to meet the increased thermal stresses that future advanced aircraft will place on currently used ester-based liquid lubricants, new lubricants will have to be developed. If a suitable replacement for ester-based lubricants cannot be found, then one must use a different lubrication method other than the current conventional method of circulating bulk lubricant (stored in a sump) through a lubricating system which contains cooling and filtering elements. Vapor phase lubrication (VPL) may be a viable alternative.

The basis for the VPL method (Ref. 1) stems from the idea that a “suitable” organic vapor can react to form a solid or semi-solid “friction polymer” compound inside moving (sliding or rolling) concentrated contact areas. Of course, it is expected that the “friction polymer” be highly lubricious and durable to minimize the frictional coefficient and wear of the contacting moving surfaces.

A review of recent literature (Refs. 2 to 5) has revealed that most of the experimental work on VPL has focused on the use of organo phosphate compounds, such as tricresyl phosphate (TCP) and tributyl phosphate, to lubricate wearing surfaces. The experimental results indicated that the phosphate compounds were successful in vapor phase lubricating certain ferrous material, i.e., cast iron, M50 steel (Refs. 3 and 4) but not nonferrous material, i.e., ceramics, Ni-based superalloys (Refs. 3 and 6). It would be highly beneficial if an organic compound could be found to vapor phase lubricate both ferrous and nonferrous components.

A class of polyphenyl thioethers, commonly called C-ethers, possess chemical properties which might make them suitable as vapor phase lubricants. They are thermally and oxidatively very stable under static conditions as shown by isoteniscope measurements and micro-oxidation tests (Ref. 7). They react, however, under boundary lubricating conditions to form insoluble organic polymeric deposits (Refs. 8 and 9). Morales (Ref. 10) investigated the decomposition of C-ethers and concluded that they behaved according to the Goldblatt polynuclear aromatic radical-anion model. In this model, C-ether decomposition, with subsequent formation of organic deposits, is related to the electron affinity (EA) of the C-ether.

A preliminary tribological study (Ref. 11) was conducted at Cleveland State University (CSU) testing a C-ether as a vapor phase lubricant in a pure sliding, reciprocating pin-on-plate apparatus. Better results were recorded when compared to similar runs using TCP. One noted drawback was that temperatures greater than 400 °C were required for the C-ether to function effectively. A low contact Hertzian pressure (1.2 MPa) was used in this study and it is believed that the C-ether could function at lower temperatures if a higher Hertzian pressure were used. Nevertheless, a vapor phase lubricant should function effectively over both a wide temperature and Hertzian pressure range.

If C-ether EA is a major factor in the formation of friction polymer under boundary lubrication, then perhaps by changing the C-ether’s EA we could lower the operating temperature where they begin to function as effective vapor phase lubricants. Adding different substituent groups to the phenyl rings of the C-ether will change its EA. A semi-empirical molecular orbital study was undertaken to assess a preliminary set of substituents which could alter the C-ether’s EA. The more promising substituents will then be incorporated into the C-ethers in future work and the resulting substituted C-ethers will be tested under tribological conditions.

CALCULATIONAL DETAILS

Optimized structures and total electronic energies of uncharged and radical anionic species were calculated using HyperChem 4.5 on a 133 MHz Pentium-based personal computer. Only AM1 semi-empirical calculations were performed using the Restricted Hartree-Fock (RHF) option, and the Unrestricted Hartree-Fock (UHF) option when needed. The convergence criterion for energy minimization was selected so that the change in total energy on successive iterations was less than 0.001 kcal/mol-Å. Electron affinities were estimated as the negative of the energy difference between the anion and uncharged molecules; no corrections for electron correlation were made. Trial calculations suggested that energy changes due to thermal effects were negligible, so such corrections were not included in the EA calculations.

Initially, diphenyl sulfide (Fig. 1) was chosen as the model C-ether of interest. The following five substituents were considered in this study: methyl, hydroxyl, fluoro, iodo, and nitro. A single substituent was added to each phenyl ring, and were sequentially attached to carbons in ortho, meta, and para positions with respect to the thio linkage. Substitution was done symmetrically, so that only three isomers for each substituent were studied. No constraints were placed on the geometries of the substituted diphenyl sulfide; conformational differences are expected to have a negligible difference on the total energies of the optimized molecules.

Similar calculations were subsequently performed on three- and four-ringed compounds that are the components of the C-ethers. Figure 1 shows the parent molecules. Substitutions with CH₃, OH, F, I, and NO₂ groups were made on the outer phenyl groups only, and again were made symmetrically on ortho, meta, and para positions with respect to the ether linkages. Estimates of the EAs were determined on the basis of the change in electronic energies; no correction for electron correlation or thermal energies were made.

RESULTS AND DISCUSSION

Table I lists the calculated EAs of the diphenyl sulfide derivatives. The parent molecule (indicated by the 'H' substituent) has a calculated EA of +126.2 kJ/mol. A literature search for its experimental value, for comparison, proved fruitless. Unless other factors (i.e., correlation effects, thermal energy changes, entropy contributions) have an overwhelming influence, the positive EA indicates an energetically-favorable process. Not unexpectedly, the

CH₃ group did not appreciably change the calculated EA, but it was surprising to see the OH group did not appreciably change the estimated EA either.

Both fluoro and iodo substituents changed the calculated EA by about the same amount, increasing it by about 30 percent. The very strongly electron-withdrawing group, NO₂, almost doubled the estimated EA to about 230 kJ/mol. While there was some effect on the EA due to position of the substituents, it was not consistent and its magnitude was probably lower than the uncertainties in the calculations.

Table II lists the summary of the calculated EAs for the four C-ether components. The reader should note that, with one exception, the only differences in the C-ether components are the types of ether linkages between the phenyl rings. The exception is the compound having only three phenyl rings, 1,3-bis(phenylthio)benzene.

The results in Table II showed interesting patterns. First of all, the predicted EAs of the parent molecules were very similar. As with diphenyl sulfide, the exact position of a substituent did not affect the predicted EA greatly. Finally, within a given substituent, the predicted EA varied very little amongst the four different C-ether molecules.

A comparison of Tables I and II showed relative similarities on the affects of the predicted EA with substitution. Both tables revealed that substitution with a CH₃ group changed the EA very little. Substitution with OH increased the EA only slightly, on average. Substitution with either I or F increased the predicted EA to about 170 kJ/mol on average. Substitution with NO₂ increases the predicted EA substantially, but more so for diphenyl sulfide than the C-ethers.

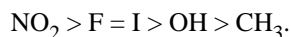
There are two immediate observations from these results. First, the effect of a substituent on the predicted electron affinity was a general one for this family of compounds, and the effect was modified little by substituent position on the phenyl rings. Second, the comparison of Tables I and II showed that the molecule diphenyl sulfide was an acceptable qualitative model for the electron-accepting abilities of C-ethers. There is some quantitative match also, but we hesitate to belabor that issue due to the variances underlying these calculations.

The results of these molecular orbital calculations clearly indicated that the NO₂, F, and I substituent groups increased the C-ether's EA by the greatest amount, whereas the CH₃ and OH groups altered the C-ether's EA only slightly. Thus, future chemical modification of the C-ethers should center on the incorporation of the NO₂, F, and I groups onto the phenyl rings of the C-ethers. Properties such as stability, toxicity, etc. must be assessed so any substituted C-ether formulation found to be unreasonably dangerous can be eliminated from VPL tests. Tribological

VPL tests on “safe” substituted C-ethers should reveal if their increased EA lowers the temperature point where they begin to lubricate effectively over a wide pressure range.

FUTURE WORK

The results of these semi-empirical molecular orbital calculations revealed that the EA of the C-ethers increased upon the addition of the following five different substituent groups (listed in order of the greatest change):



The NO_2 , F, and I groups will be added to the phenyl rings of the C-ethers, to increase their EA, and tribological VPL tests will be conducted (on the “safe” formulations) to assess their lubricating effectiveness. In addition, further molecular orbital calculations will be performed on a different set of substituents including $-\text{CF}_3$, $-\text{OCH}_3$, and $-\text{SCH}_3$.

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TABLE I.—ELECTRON AFFINITIES IN
kJ/MOLE FOR MODEL DIPHENYLSULFIDE


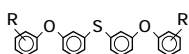
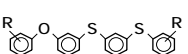
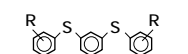
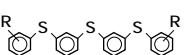
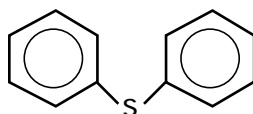
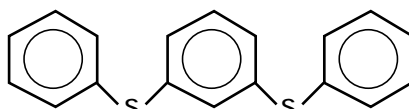
Position	R equals	
	H	126.2
Ortho— Meta— Para—	OH OH OH	128.5 141.7 136.9
Ortho— Meta— Para—	CH ₃ CH ₃ CH ₃	125.6 125.3 125.8
Ortho— Meta— Para—	I I I	149.2 168.8 173.2
Ortho— Meta— Para—	F F F	171.4 166.1 163.2
Ortho— Meta— Para—	NO ₂ NO ₂ NO ₂	223.3 237.4 254.3

TABLE II.—ELECTRON AFFINITIES IN kJ/MOLE FOR C-ATHERS

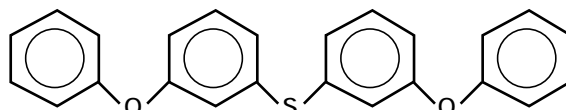
Position	R equals				
	H	151.1	152.4	139.2	153.6
Ortho— Meta— Para—	OH OH OH	152.5 157.8 154.5	155.6 162.9 154.8	142.9 153.8 146.8	148.9 160.8 155.6
Ortho— Meta— Para—	CH ₃ CH ₃ CH ₃	150.6 149.6 150.3	152.1 151.5 151.3	141.9 140.7 141.0	153.6 152.3 152.5
Ortho— Meta— Para—	I I I	164.7 168.0 169.6	163.5 165.7 170.7	149.5 167.2 171.9	183.8 174.2 171.9
Ortho— Meta— Para—	F F F	164.2 168.7 167.5	165.8 170.1 168.9	168.4 169.1 167.2	166.6 171.4 170.3
Ortho— Meta— Para—	NO ₂ NO ₂ NO ₂	211.5 199.6 203.9	193.9 202.1 204.3	206.8 214.6 224.7	217.2 225.2 231.5



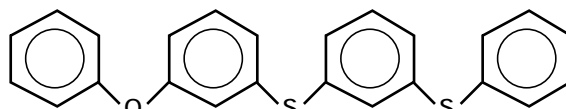
Diphenyl sulfide



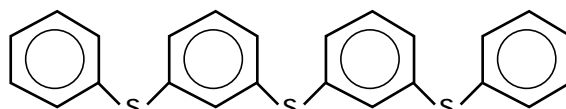
(a)



(b)



(c)



(d)

Figure 1.—Chemical composition of diphenyl sulfide and components of C-ether. (a) 1,3-bis(phenylthio)benzene; molecular weight, 294. (b) 1,1-thiobis[3-phenoxybenzene]; molecular weight, 370. (c) 1-phenoxy-3-[[3-(phenylthio)phenyl]thio]benzene; molecular weight, 386. (d) 1,1-thiobis[3-(phenylthio)benzene]; molecular weight, 402.

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Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE November 1997	3. REPORT TYPE AND DATES COVERED Technical Memorandum		
4. TITLE AND SUBTITLE Electron Affinity Calculations for Thioethers		5. FUNDING NUMBERS WU-523-22-13-00		
6. AUTHOR(S) Deley L. Sulton, Michael Boothe, David W. Ball, and Wilfredo Morales				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191		8. PERFORMING ORGANIZATION REPORT NUMBER E-10942		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001		10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA TM-113178		
11. SUPPLEMENTARY NOTES Prepared for the 1998 Annual Meeting sponsored by the Society of Tribologists and Lubrication Engineers, Detroit, Michigan, May 17-21, 1998. Deley L. Sulton, Michael Boothe and David W. Ball, Cleveland State University, Cleveland, Ohio 44115; Wilfredo Morales, NASA Lewis Research Center. Responsible person, Wilfredo Morales, organization code 5140, (216) 433-6052.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified - Unlimited Subject Categories 23 and 27 Distribution: Nonstandard This publication is available from the NASA Center for AeroSpace Information, (301) 621-0390.			12b. DISTRIBUTION CODE	
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14. SUBJECT TERMS Thioethers; Molecular orbital calculations; Electron affinity; Vapor phase lubrication			15. NUMBER OF PAGES 14	
			16. PRICE CODE A03	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	